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published in

NIC Symposium 2006 ,
G. Münster, D. Wolf, M. Kremer (Editors),
John von Neumann Institute for Computing, Jülich,
NIC Series, Vol. **32**, ISBN 3-00-017351-X, pp. 57-64, 2006.

http://www.fz-juelich.de/nic-series/volume32

Understanding Mechanically Induced Chemical Reactions

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We have used high level computer simulations to investigate modification of the chemical reactivity of molecules under tensile stress. The application of a mechanical force can affect the electronic structure and steric protection, opening up unexpected reaction pathways. These phenomena have implications for the interpretation of single molecule atomic force microscopy experiments which investigate the forced rupture of polymers, and the chemical basis of material failure under a mechanical load.

1 Introduction: Improving Material Performance

The demand for new advanced materials, which while remaining stable over a range of physical and chemical conditions are also non-toxic and can be produced efficiently, is constantly challenged by the development of new technologies. Understanding how materials respond in different environments to mechanical manipulation on the molecular level is essential for the improvement of performance and adaption for new applications. The advent of single molecule experiments combined with high level computer simulations examine modified chemical processes which can occur in a material subjected to extreme mechanical and environmental conditions.

Siloxanes are inorganic polymers with a flexible backbone made up of alternating silicon and oxygen atoms, with bulky methyl groups attached to the silicon atoms (fig.1). Their high flexibility and durability, and stability at high and low temperatures leads to their application in a wide range of situations as adhesives, coatings, sealants and lubricants. From aerospace down to microelectronics on account of their insulating and optical properties, and medical applications because of their non-toxicity, they are an important class of material for situations where mechanical strength and resistance to chemical degradation play a crucial role. To understand the chemical basis of their strength, a collaboration combining single molecule atomic force microscopy (AFM) with quantum chemistry simulations seeks to characterize stress induced bond rupture processes.

2 Understanding Single Molecule Atomic Force Microscopy

Single Molecule AFM[1,2] has principally been used to investigate weak interactions in biological systems[3,4], but can also be used to investigate stronger covalent binding in synthetic materials. In a single molecule AFM experiment a single polymer is pulled from a substrate by an AFM tip until one of the bonds, either in the polymer backbone, at the attachments, or within the substrate is ruptured yielding a force curve and rupture force, the magnitude of which being dependent on the strength of the disrupted interaction. Grandbois and coworkers[5] found the rupture force corresponding to a covalent silicon - carbon bond at the

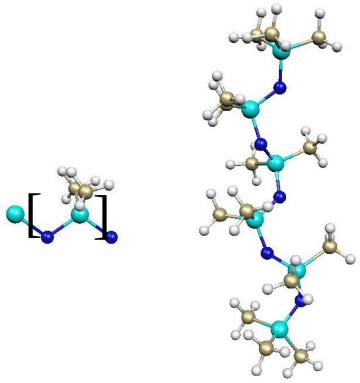

Figure 1. The siloxane monomer (left) and the equilibrium geometry of the siloxane hexamer (right). Turquoise: silicon, blue: oxygen, gold: carbon, white: hydrogen.

attachment of a polysaccharide polymer to an amylose functionalized silica substrate to be 2.0 ± 0.3 nN. In order to identify the breaking bond within the system, static quantum chemistry calculations[6,7] were used to compared the strengths of different possible bonds at the attachment. Scenarios in which the strength of a synthetic single molecule have also been investigated are that of a knot in a polyethylene molecule[8–10] and a study of a thiol molecule pulled from a gold surface[11], both investigated using first principles molecular dynamics simulations. While simulating systems representing AFM experiments, the strength of polymers has been found to be dependent on pulling rate and oligomer length[12] and the solvent surrounding the stretched molecule[13] using Car-Parrinello molecular dynamics simulations. In order to correctly interpret the experimental force curves, theoretical investigations of the systems are necessary to identify the breaking bond, the chemical mechanism of rupture, the influence of solvent and other species in the surrounding environment, and the surface / tip attachment. It is these issues which we address in this study of siloxane rupture taking into account the possible modifications of the chemical reactivity caused by the application of tensile stress. We also seek to determine how the single molecule behavior relates to processes in the bulk siloxane elastomer subjected to a mechanical load.

3 Simulating Molecules under Stress

We use first principles molecular dynamics simulations (Car-Parrinello Molecular Dynamics[14,15]) where a full calculation of the electronic structure using density functional theory[16,17] is performed 'on the fly' for each step of a molecular dynamics trajectory. Using the parallel computing facilities at the John von Neumann Institute for Computing, Jülich, we can follow the evolution of the electronic structure of systems containing up to 300 atoms on a timescale of the order of a few picoseconds at room temperature. In the experiments a siloxane elastomer is covalently attached between a silica substrate and silica tip and pulled in a hexamethyldisiloxane (HMDS - the siloxane dimer) solvent. In the sim-

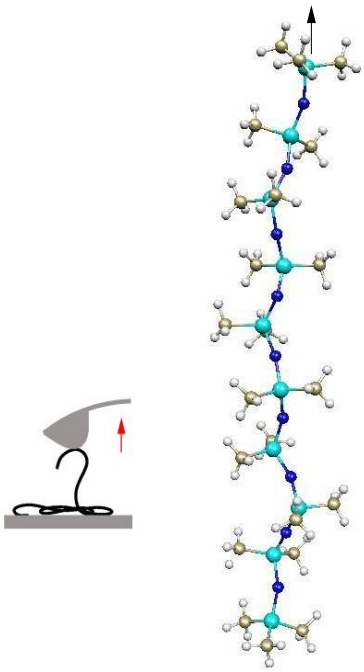

Figure 2. The diagram shows the siloxane decamer (ten silicon atoms in the backbone) in the simulation. The lower terminal silicon atom is fixed and the opposite terminal silicon atom is pulled at a predefined rate in the direction indicated by the arrow so applying a tensile stress to the molecule. The inset shows a schematic representation of the AFM set up with one molecule attached between a substrate and tip.

ulations siloxane oligomers of varying lengths (containing up to ten silicon atoms in the backbone) are pulled at varying rates in different environments to describe the high force regime of the AFM experiment (fig. 2). The mechanically induced rupture process can be characterized and the factors which determine which covalent bond breaks assessed. This information is then used to assign the mechanically measured rupture force.

4 Bond Rupture in the High Force Regime

The ways in which the siloxane elastomer can respond to an applied stress are shown for the siloxane decamer (10 silicon atoms in the backbone) in fig.3. The high flexibility of the molecule stems from the easy deformation of the Si-O-Si bond angle shown in 3 i), which can take values up to 180^O, allowing the polymer to be considered as a chain of spaced silicon atoms. The average values of the stiffer O-Si-O bond angle and Si-O bond length increase simultaneously and it can be seen in 3 ii) and iii) that although extreme values for individual angles and bond lengths can occur, the siloxane does not rupture until a threshold molecular extension has been reached.

The evolution of the electronic structure can be followed as the molecule is stretched and is visualized with localized electron orbitals as shown in fig.4. As the molecule is

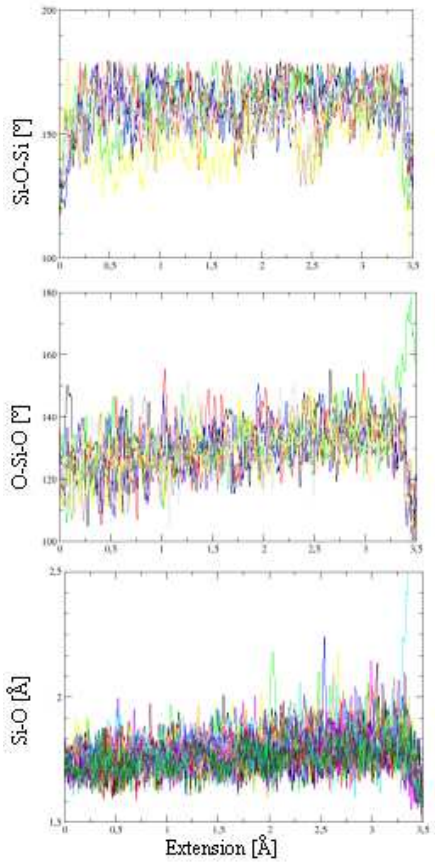

Figure 3. The response of the siloxane decamer to tensile stress, each colour represents a different bond angle or bond length as indicated in the polymer backbone. i) shows the flexibility of the Si-O-Si bond angle which can take values up to 180^o in the simulations. ii) shows how the average value of the stiffer O-Si-O bond increases. iii) shows the increase of the average Si-O bond length. Although individual bonds can reach values of over 2.0Å, the siloxane does not rupture until the total extension has reached a threshold value[18].

stretched the Si-O-Si bonds become polarized, then an Si-O bond breaks via an ionic mechanism, whereby a negative charge is left on the oxygen atom and a positive charge on the silicon, and finally proton transfer occurs from a methyl group to the negatively charged oxygen to neutralize the products. In the case of the longer oligomers (hexamer and decamer), the charged fragments recede rapidly to their coiled equilibrium geometries before proton transfer can occur leaving charged species in the system. The force required to rupture a covalent silicon - oxygen bond can be calculated from the simulations and is shown to be dependent on the pulling rate and oligomer length: slower rates and longer oligomers lead to lower forces. We have calculated a rupture force of 4.4 nN for a siloxane decamer pulled at 55 m/s[18] which is an upper bound for the force as the experimental elastomers are longer and the pulling rates slower.

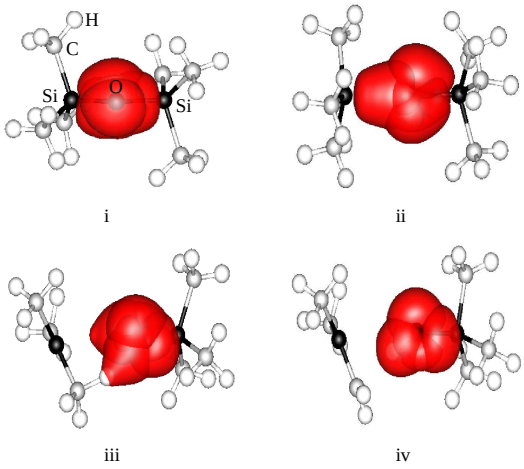

Figure 4. The localized orbitals (Wannier functions) of the electrons in the Si-O-Si backbond of the siloxane dimer. i) shows the equilibrium starting electronic structure. ii) shows the polarization as the molecule is stretched. iii) shows the rupture of an Si-O bond. iv) shows the proton transfer which neutralizes the rupture products[18].

The computer simulations show that the siloxane oligomers are highly flexible and efficient at quickly distributing strain throughout the molecule. Once ruptured, either proton transfer can occur depending on the immediate surroundings to neutralize the products, or charged species are formed which could react further. Both outcomes have implications for understanding the origins of stress induced material failure[18].

5 Mechanically Induced Chemistry: Interaction with the Environment

As the siloxane elastomer is stretched the silicon - oxygen bonds become polarized, leading to local concentrations of charge in the backbone, and the backbone becomes more exposed as the methyl groups surrounding it become more spread out (fig. 2). This could alter the reactivity of the normally inert siloxanes under tensile stress and open up new reaction pathways with species in the surroundings. We are currently investigating possible reactions with solvent molecules as used in the single molecule atomic force microscopy experiments, and with trace amounts of water which could play a role in material failure using computer simulations.

The solvent used in the experiments is hexamethyldisiloxane (HMDS - the siloxane dimer) and we are simulating the stretching of a siloxane oligomer surrounded by HMDS molecules at an appropriate density(fig. 5). Although there is no attraction between the species if no force is applied to the elastomer, in its stretched state the polarized Si-O bond and the exposure of the backbone aid the close approach of a solvent molecule. During our simulations no attraction or interaction between the species was detected, their close approach being hindered by the methyl groups, and so the solvent should not influence the outcome of the experiments.

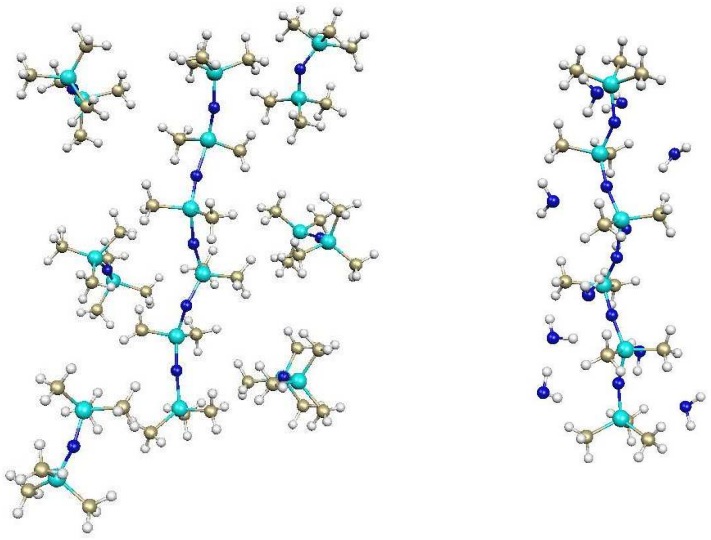

Figure 5. The left hand figure shows the stretched siloxane hexamer surrounded by HMDS solvent molecules during a simulation at an appropriate density. The right hand figure shows the siloxane hexamer surrounded by water molecules, the simulation is to determine whether a water molecule can approach the siloxane and cause its rupture.

We are also studying the influence of water on the rupture reaction mechanism. This protic solvent could attack the polarized Si-O bond before the maximum extension has been reached, resulting in lower measured rupture forces.

6 Pulling Elastomers from Silica

We have started simulating the pulling of a siloxane elastomer from a silica surface (fig. 6). In the sinlge molecule atomic force microscopy experiments a siloxane polymer is covalently bound between a silica substrate and silica AFM tip and our simulations model what is happening at the attachment bonds as the polymer is pulled away from the surface. The substrate, attachment and siloxane molecule are all systems containing covalent silicon - oxygen bonds: but which bond is most likely to break in the experiment and to what extent can the substrate be deformed? Our simulations will show which bond is most likely to break and identify the factors which determine which bond will break, allowing the experiment to be tuned into investigating specific interactions.

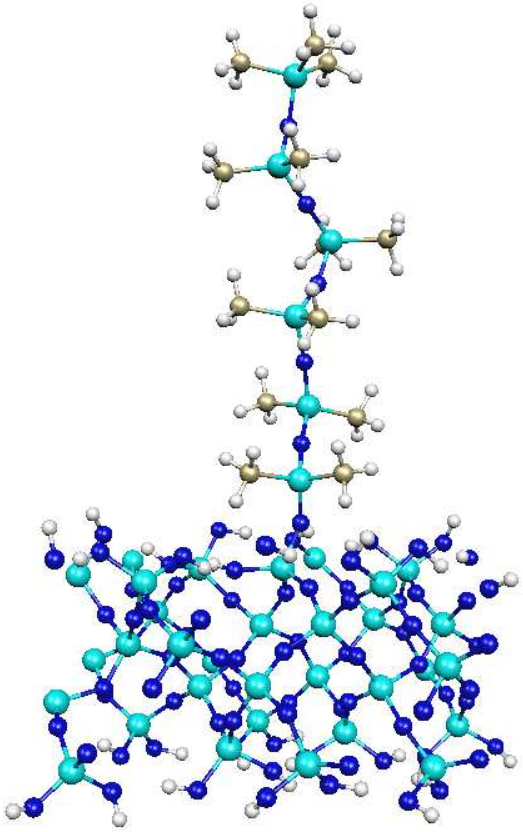

Figure 6. The siloxane hexamer pulled from a silica surface.

7 Conclusions: Implications of Mechanically Induced Chemistry for the Elastomer under Stress

Our simulations have shown how the application of a tensile stress to siloxane elastomers can alter their chemical reactivity by modifying their electronic structure and altering the steric protection of bonds thereby opening up new reaction pathways. We can identify and describe chemical rupture mechanisms as probed in single atomic force microscopy experiments to identify the factors which determine the strength of an individual molecule. We are also performing calculations to understand how reaction fragments can react with one another in the bulk siloxane. Understanding rupture processes is key to identifying the mechanisms which lead to permanent deformation and ultimate material failure in elastomers. The modified chemistry of the stretched polymer therefore plays an important role in the behavior of materials under stress and in developing ways to enhance material performance.

Acknowledgments

This work is carried out as part of a cooperation between the Institute for Physical Chemistry (Chair: Prof. C. Bräuchle) at the Ludwig Maximilians University in Munich, and Wacker Chemie, Burghausen. We are indebted to the John von Neumann Institute for Computing in Jülich for computing time on the Jump cluster. We have also used resources at the Leibniz Rechenzentrum in Munich.

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